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CHEMISTRY DIVISION

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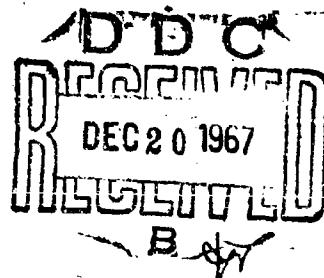
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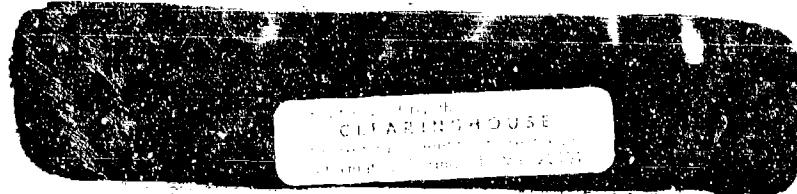
A STUDY OF THE ORGANIC VAPORS IN THE ATMOSPHERE
OF THE USS SKATE

by

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ABSTRACT

A study of the trace organic contaminants in the atmosphere of the USS SKATE was carried out aboard ship by means of both gas chromatography and a catalytic combustion technique. The hydrocarbon contaminants were concentrated by a backflush technique and chromatographed directly without recourse to carbon sampling. Integration of the areas under the chromatograms obtained indicated substantially higher concentration of hydrocarbons, especially in the C_8 and lower molecular weight range, than were measured by Dorex carbon canisters exposed simultaneously. An examination of the effluent from Dorex canisters during exposure showed a high leakage of hydrocarbons through the carbon bed. Many of the hydrocarbons detected have been tentatively identified by a comparison of retention volumes with known standards.

PROBLEM STATUS

This is an interim report; work on the problem is continuing.

AUTHORIZATION

A STUDY OF THE ORGANIC VAPORS IN THE ATMOSPHERE OF THE USS SKATE

INTRODUCTION

The atmospheres of nuclear submarines are known to contain a large number of organic compounds as contaminants, only a few of which have been identified (1). The importance of identifying these substances and controlling their atmospheric concentrations is obvious from a toxicological standpoint. Although the bulk of these organic contaminants have been shown to be hydrocarbons (2), relatively nontoxic at the concentrations normally found aboard ships (1), analytical data for the more toxic aromatic hydrocarbons would be desirable. Aside from toxicological effects, the elimination of atmospheric hydrocarbons is advantageous for other reasons. With the methods of analysis now used hydrocarbons may mask the presence of low levels of much more noxious substances. Also, it has been pointed out that combustion in the CO/H_2 burner of the concentrations of hydrocarbons now existing in the atmospheres of nuclear submarines consumes as much oxygen as several men (3). Thus a decrease in the hydrocarbon content of the air would effectively increase the oxygen endurance of the submarine.

The most successful techniques for studying atmospheric hydrocarbons have been infrared spectroscopy (4) and gas chromatography in conjunction with carbon sampling (2,5). At present, the hydrocarbon content of nuclear submarine air is determined routinely by a program of sampling with Dorex carbon canisters. Although much valuable information has been obtained in this manner, questions have arisen as to the exact qualitative and quantitative significance of the results.

A procedure in which carbon is not used as a sampling medium would be desirable for both the measurement of total hydrocarbons and the determination of individual components. It is conceivable that the material desorbed from carbon canisters is not truly representative of the substances present in submarine air. Some components could be eluted during the sampling period itself, especially in view of the extremely large volume of air that must be passed through the canister in order to obtain a measurable quantity of organic material. Since the desorption step requires temperatures of 300-400°C, compounds adsorbed on the carbon could be changed chemically. Other compounds might be held so firmly that they would not be recovered even at these temperatures.

The prime objective of the trip aboard the USS SKATE was to test the feasibility of determining contaminants in submarine air directly by means of a highly sensitive gas chromatograph, the Pye Argon Chromatograph. A reversible concentration technique based upon chromatographic principles was used to increase the vapor concentration of these contaminants to a suitable level for chromatographic study. The advantages of such a procedure for handling air samples are threefold: (1) many of the uncertainties arising from carbon sampling are eliminated, (2) the required sampling time is a few minutes rather than several hours and (3) selective sampling and analytical chromatographic columns may be used for the discrimination of a wide variety of compounds.

A comparison method for the determination of total organic combustibles in the atmosphere by catalytic combustion to CO_2 and the subsequent CO_2 determination by infrared absorption was tested aboard ship and showed many promising aspects.

The trip aboard the USS SKATE afforded an excellent opportunity to study atmospheric contaminants under closed-ship conditions. The USS SKATE dove at 1800 on 19 October 1959, surfaced briefly for 45 minutes at noon the following day and then remained submerged until 1300, 31 October 1959.

EXPERIMENTAL PROCEDURES AND PRELIMINARY EXPERIMENTS

The Pye Argon Chromatograph is capable of sensitivities 10,000 to 100,000 times greater than those obtained from the usual thermal conductivity detectors. This extremely high sensitivity is obtained by the use of the Lovelock ionization detector that uses argon as the carrier gas (6). Argon atoms flowing through the detector are excited to a metastable electronic state at 11.6 e.v. by a radioactive source (radium D, strontium 90 or tritium). The subsequent collision of an excited argon atom with a molecule having an ionization potential of less than 11.6 e.v. results in the ionization of that molecule. Voltages of 750 to 2000 v. are impressed across the electrodes of the detector and the ionization current provides a measure of the amount of foreign molecules in the argon. Fortunately, most organic compounds, with the exception of methane, ethane, ethylene and certain halogenated derivatives, have ionization potentials of less than 11.6 e.v. making the detector most suitable for their determination. Most permanent gases have higher ionization potentials, consequently the detector is insensitive to their presence.

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Substances with ionization potentials above 11.6 e.v. that contain atoms capable of acting as electron acceptors, e.g., oxygen and water, decrease the ionization current by electron capture. This effect is noticeable as a pronounced decrease of response to other substances simultaneously passing through the detector. Traces of water or oxygen arising from leaks in the carrier gas system or introduced with the sample can reduce the detector sensitivity by a factor of several hundred. Water is particularly bad in that it is strongly adsorbed on the solid support and is released slowly thereby interfering with the analysis of other constituents.

The Pye chromatograph uses a 4 mm I.D. x 4 ft straight glass column packed with a liquid partitioning agent adsorbed on the surface of an inert solid. Columns used aboard the USS SKATE contained either squalane, a good partitioning agent for hydrocarbons, or polyethylene glycol (average molecular weight 400), a selective agent for aromatic hydrocarbons and oxygenated compounds, both adsorbed on Chromosorb.* Squalane columns contained five parts squalane and two parts polyethylene glycol 400 per 100 parts Chromosorb; polyethylene glycol columns, 30 parts of the glycol to 100 parts Chromosorb. Atmosphere samples were chromatographed at various temperatures between room temperature and 100°C with a carrier gas flow rate of about 20 ml/min.

Previous chromatographic work at this Laboratory has shown that the Pye gives good response to several parts per million of a pure hydrocarbon in air. Since the hydrocarbon contaminants in nuclear submarine atmospheres consist of many hydrocarbons with combined concentrations as low as several parts per million, the Pye's sensitivity is just below that required for handling direct air samples. In dealing with gas samples, not only the absolute amount of hydrocarbon but also the volume of the sample is important. As the sample size increases beyond a few milliliters, the width of the chromatographic peaks increases and resolution suffers. Figure 1 illustrates the effect of sample volume upon the resolution of n-heptane and cyclohexane, compounds chosen because they are not completely resolved under ideal conditions of sample introduction. The amount of hydrocarbon represented by each chromatogram is approximately the same, 0.5 mmg,** only the dilution in air varies. Since chromatographic peaks increase in width with increasing retention

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*Chromosorb - A registered trade name of Johns-Manville for a specially treated diatomaceous earth.

** mmg - microgram.

time, a small sample volume is particularly important for the resolution of the early, normally very sharp, peaks. From Figure 1 it can be seen that the sample volume cannot be much larger than ten milliliters if peaks with the retention times of n-heptane and cyclohexane are to be resolved.

Advantage was taken of the change of retention volume as a function of temperature to concentrate low levels of hydrocarbons in air to a suitable concentration for chromatographic study. Retention volume (V_R), the volume of carrier gas that is required to elute a substance from a chromatographic column, is a characteristic constant of a substance under constant conditions of column temperature, composition and quantity of the partitioning agent, column length and pressure drop across the column. Retention volume decreases exponentially with temperature. The change of retention volume with temperature may be calculated approximately by using an expression similar to the Clausius-Clapeyron equation:

$$\ln \frac{V_{R2}}{V_{R1}} = \frac{\Delta H_v}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

where

V_{R1} = Retention volume at temperature T_1

V_{R2} = Retention volume at temperature T_2

ΔH_v = Heat of vaporization

R = Gas constant

For this expression to be applicable, it must be assumed that the substance forms an ideal solution with the stationary phase, that is, its heat of solution in the partitioning agent is the same as its heat of vaporization and that this heat is constant over the temperature range T_1 to T_2. Simplifying assumptions must also be made that the interstitial gas volume of the column and the liquid volume of the partitioning liquid do not change with temperature.

If a sample of a substance at a low concentration in air is passed through a partitioning column at a given temperature, the substance will be retained completely by the column if the sample volume is less than the retention volume of the substance at that temperature. If now the column is heated to a higher temperature and backflushed, the substance will be completely desorbed from the column in a lesser volume than

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the original sample size since its retention volume is smaller at the higher temperature. The low temperature sorption of the material and the higher temperature desorption increases the vapor concentration of the substance by the ratio of the retention volumes at the two temperatures. Table 1 lists experimental values of the retention volumes at 0° and 100°C for some hydrocarbons in a four foot squalane column. It also compares the observed ratios of retention volumes at the two temperatures with those calculated from the above relation. Values of V_R in Table 1 are measured to the peak maxima. The ratio of the retention volume for the initial emergence of the peak at the lower temperature to the final retention volume of the tail at the higher temperature should give a more precise value of the concentration factor but the difference is small when efficient columns are used.

The concentration step may be illustrated by considering the values for 2,2-dimethylbutane from Table 1. The retention volume for this hydrocarbon at 0°C in a four foot squalane column is 1570 ml; that is, a sample introduced at one end of the column at 0°C will emerge from the other end when 1570 ml of gas have passed through the column. If a 300 ml sample of air containing a low concentration of 2,2-dimethylbutane is passed through the column the hydrocarbon will be contained in approximately the first one fifth of the column since the gas passed through the column is about one fifth the retention volume. The effect of the pressure drop across the column is neglected. n-Pentane (V_R = 970) in a similar 300 ml air sample would be contained in a little less than the first third of the column. Thus the length of the column penetrated by a hydrocarbon depends entirely upon its retention volume, the smaller this volume, the greater the penetration. The sample volume must not exceed the retention volume of any component to be determined or a portion of that component will be eluted from the column.

Heating the column containing the collected sample to 100°C and passing a gas through the column in the opposite direction elutes the sample in a smaller volume of gas than the original air sample. In the case of 2,2-dimethylbutane, the 100° increase in temperature decreases the retention volume to 62.5 ml. Since the sample was collected at 0° in the first one fifth of the column, the eluted material has only to traverse this distance in the backflush step and hence is eluted in about 12 ml of gas. The vapor concentration of the 2,2-dimethylbutane has been increased about twenty-five times. Higher boiling materials with large retention volumes at 100° are eluted in about the same volume of gas because of the short distance that they penetrate the

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column at 0°C. As shown in Table 1, better concentration efficiencies are obtained for these higher boiling compounds because of their larger heats of vaporization.

The temperatures of 0° and 100°C were chosen for the collecting and backflushing steps for convenience in shipboard use. A greater temperature difference, especially a lower collection temperature, would of course increase the efficiency of the process. The solidification point of the stationary liquid limits the lower temperature that can be used unless the temperature is low enough to completely freeze out the sample in the first portion of the column.

The apparatus used for sample concentration is illustrated schematically in Figure 2. The concentrating column consisted of a coiled length of 1/4 in. O.D. copper tubing fitted with needle valves and stainless steel ball joints at each end. A four foot length of the coil was packed with the partitioning agent, either squalane or polyethylene glycol 400, 3 parts by weight to 10 of Chromosorb. Preliminary laboratory work showed that small samples of polar materials such as oxygenated compounds were either completely adsorbed or retained for long periods of time by surface adsorption on the Chromosorb in squalane columns. To eliminate this residual adsorptive capacity, two percent of the highly polar polyethylene glycol 400 was added to the Chromosorb used in squalane columns aboard ship (7).

The sampling coil was immersed in an ice bath for several minutes prior to and during the sample collection. A known volume of air was pulled through the coil with a small pump, the sample size controlled by the flow rate and pumping time. After closing the needle valves, the coil was immersed in a boiling water bath and connected in series with the analytical column in the Pye chromatograph. Upon equilibration of the coil with the water bath, the valves were opened to resume the argon flow and backflush the sample into the chromatograph.

Because of the desensitizing action of water on the detector, it was necessary to dry the samples before introduction into the chromatograph. Various common desiccants tested either had enough surface activity to interfere or were not sufficiently effective for water removal. A short tube containing glycerol adsorbed on Chromosorb (3:10) inserted between the sampling and analytical columns proved fairly satisfactory. Although the glycerol did not irreversibly absorb water, it retained it until the bulk of the sample had passed through the detector.

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Table 1

Effect of Temperature on Retention Volumes of Hydrocarbons

Column: Squalane on Chromosorb (3:10), 1/4 in. x 4 ft

Compound	B.P.($°C$)	$V_R 0°$(ml)	$V_R 100°$(ml)	$V_R 0°/V_R 100°$ (Exp.)	$V_R 0°/V_R 100°$ (calc.)
1-Pentene	30.0	805	38.8	20.7	--
n-Pentane	36.1	1004	43.6	23.0	--
2,2-Dimethylbutane	49.7	1451	61.1	23.8	23
n-Hexane	68.7	3620	99.4	36.4	34
n-Heptane	98.4	--	240.0	--	62

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Preliminary laboratory studies of the concentrating technique showed that backflush-concentrated samples of paint thinner, originally seven parts per million in air, yielded chromatograms identical to those from higher vapor concentrations chromatographed directly.

Assuming that the maximum sample volume consistent with good resolution is ten milliliters as it enters the chromatograph, the air sample before concentration must not exceed 200 to 600 ml, depending upon the substance to be determined. This is based upon the expected concentration increases by backflushing predicted by the data of Table 1. Sample volumes of 300 ml of the USS SKATE atmosphere were sufficient for good detector response.

A similar concentration method was tested aboard the USS SKATE to measure the total combustibles, excluding methane, in the atmosphere by sorption in a cold column followed by elution at boiling water temperature, combustion to CO_2 and measurement of the CO_2 by infrared absorption. The amount of total combustibles thus found was to be compared to the total of individuals identified by gas chromatography and with the results of carbon canister samples.

The apparatus was not sufficiently refined to accomplish the objective successfully. Several problems arose in implementing the plan. Because of the high background CO_2 (1.0-1.3%) in the ship's atmosphere this gas had to be removed or compensated for. It was found that flushing the CO_2 through the column in which the combustibles were absorbed drove these materials further into the column resulting in broadened peaks upon elution. Another problem which arose was the apparent production or release of combustibles from the squalane or polyethylene glycol used as the stationary phase in the column when the column was heated at boiling water temperatures. This resulted in a non-reproducible base line.

A procedure whereby submarine air was continuously passed through a CO_2 absorber (Caroxite) and thence through a furnace containing Hopcalite at 420-440°C and the resulting CO_2 measured seemed to work well. Carbon dioxide measurements were made with a Liston-Becker Infrared Model 15A Analyzer. The data obtained by the combustion method during this voyage were encouraging and consequently further laboratory study of this method of analysis is planned.

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RESULTS AND DISCUSSION

Sample Concentration Technique

The backflush technique concentrated the hydrocarbon contaminants in air samples of the USS SKATE atmosphere to a suitable level for their chromatographic determination. Figure 3 shows the response obtained from a 20 ml air sample from the forward torpedo room chromatographed directly. Only a few small peaks due to hydrocarbons present in the highest concentrations are seen. Figure 4 is a chromatogram of a 300 ml sample of engine room air subjected to the concentration procedure. A marked increase in response can be seen; the first portion of the curve, through Peak 18, was attenuated three times over Figure 3. A chromatogram of the organic liquid desorbed from a carbon canister exposed during the trip is shown in Figure 5. All three of these curves were produced with a squalane column at 75°C.

A comparison of Figures 4 and 5 reveals that the curves obtained from air samples concentrated by backflushing do not show the sharp peak resolution obtained from liquid samples. This lack of resolution is most obvious in the separation of the early peaks. Figure 4 also demonstrates the masking of the first few hydrocarbon peaks by the excessively wide air peak due to residual air in the collecting column. The first three peaks in Figure 5 are not present in Figure 4. A very high concentration of hydrocarbon is required to override the desensitizing effect of air on the detector.

The concentrating apparatus used aboard the USS SKATE was crude. A few relatively simple refinements should greatly improve the concentrating efficiency. Decreasing the dead volume between the concentrating column and the analytical column in the chromatograph should tend to sharpen the peaks by decreasing mixing in the gas phase. Lower sampling and higher backflushing temperatures should introduce the sample to the chromatograph in a smaller volume and thus greatly improve resolution. Such temperatures could easily be obtained aboard ship by using an ice-salt cooling bath and an electric heater for backflushing. A lower sampling temperature also would permit determination of lower molecular weight hydrocarbons that are not completely retained by the sampling coil at 0°C. A valving arrangement whereby air could be flushed completely from the system after the cold collecting column is placed in series with the chromatograph would eliminate its interference.

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Nature of the Hydrocarbons Found in the USS SKATE Atmosphere

Figure 6 is a chromatogram of a sample of paint thinner for comparison purposes. Similar peaks were obtained from both the paint thinner and the USS SKATE atmosphere but the quantitative distribution of components differed.

Air samples, after concentration, were chromatographed at various column temperatures from 27° to 100°C to determine the effect of temperature on the separation and to see if low molecular weight hydrocarbons could be detected with low column temperatures. A column temperature of 100°C did not provide adequate resolution to be generally useful but did show that the relative amount of material with longer retention volumes than Peak 24 (tentatively identified as n-undecane) of Figures 4 and 5 was very small. A temperature of 75°C was generally useful for comparison purposes. It provided an analysis time of less than three hours but did not separate some of the lower boiling hydrocarbons from air. Experiments at 50°C and at room temperature (Figures 7 and 9) yielded better separations but required much longer analysis times. Figures 8 and 10 are chromatograms of the oil phase steamed from a carbon canister and chromatographed under similar conditions to those used for the air samples. Peaks obtained from the oil samples are numbered consecutively at each temperature. Corresponding peaks at each column temperature from the air samples are denoted by the same number. A letter in parentheses following a peak number indicates peaks produced by the same hydrocarbon at the different temperatures used. Thus Peak 19(i) at 27°C (Figures 8 and 9), most likely due to a mixture of m- and p-xylenes, corresponds to Peak 15(i) at 50°C (Figures 6 and 7) and to Peak 9(i) at 75°C (Figures 3 and 4).

The improved separation obtained at lower column temperatures may be seen by a comparison of Figures 4, 7 and 9. Peak 17 at 75° (Figure 4) was separated into three, Peaks 8, 9 and 10, at 50° (Figure 7) and into six, Peaks 10 to 15, at 28°C (Figure 9). This again serves to point out the complexity of the hydrocarbon mixture in the atmosphere of nuclear submarines. Even at room temperature, complete separation of the hydrocarbon contaminants from air was not achieved. Peak 1 in Figure 8 is probably due largely to n-hexane indicating that peaks appearing earlier must be due to lower boiling hydrocarbons, probably branched hexanes or pentanes. The presence or absence of hydrocarbons of lower molecular weight could not be established with the columns and conditions used during this trip.

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A few experiments with a polyethylene glycol 400 column indicated the presence of methyl and ethyl alcohols in varying quantities in the atmosphere. This was not unexpected since these air samples were taken in the forward torpedo room where ethyl alcohol was used from time to time and a duplicating machine using these alcohols was not far from this compartment. It was hoped to learn more about the presence of oxygenated compounds and aromatic hydrocarbons with this partitioning agent but its selectivity for these materials was not great enough to deal with the complex mixture at hand.

The complexity of the hydrocarbon mixture in submarine atmospheres is to be expected in view of the many individual hydrocarbons that make up any petroleum fraction that might serve as a source of air contamination. However, an examination of analytical data dealing with the composition of petroleum (8) showed that a relatively few hydrocarbons generally account for a high percentage of most fractions, especially in the volatility range of those found in submarine air. Even though petroleums from different geographical sources vary widely in the amount of the different types of hydrocarbons that they contain, such as normal paraffins, cycloparaffins and aromatics, the distribution of individual hydrocarbons in each class does not vary nearly so much.

The retention volumes of some selected hydrocarbons, chosen because of their reported abundance in the proper fractions of several petroleums (8), were compared with those obtained from submarine air. Each hydrocarbon tested matched an unknown, often very prominent, peak in the chromatograms of the atmospheric contaminants. Table 2 lists the hydrocarbons tested and correlates them with the chromatographic peaks by means of the letters in the first column. Relative retention volumes are listed only where those of the hydrocarbons and unknown peaks matched at the column temperature indicated. Blanks in the table indicate only that the pure hydrocarbons have not yet been chromatographed at that temperature and does not indicate a lack of correlation with the unknown peaks. Many of these hydrocarbons, especially the aromatics, have already been qualitatively identified in nuclear submarine atmospheres (1,4). Other hydrocarbons reported to be among the more common in petroleum will probably account for the remaining large peaks when samples of the pure hydrocarbons are obtained for comparison.

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Table 2

Tentative Identification of Chromatographic Peaks Obtained from Atmosphere of USS SKATE

Peak	Hydrocarbon	Relative Retention Volume (n-Heptane=1.00)		
		75°C	50°C	28°C
a	n-Hexane	--	0.366	0.238
b	Benzene	--	0.704	0.632
c	n-Heptane	1.00	1.00	1.00
d	Methylcyclohexane	1.33	--	--
e	Toluene	1.90	1.89	1.80
f	n-Octane	2.33	2.70	3.05
g	Ethylcyclohexane	3.50	3.76	--
h	Ethylbenzene	4.07	4.51	--
i	m,p-Xylene	4.60	5.25	5.85
j	o-Xylene	5.67	6.44	7.19
k	n-Nonane	5.67	7.21	9.18
l	Isopropylbenzene	6.60	7.86	--
m	n-Propylbenzene	8.33	--	--
n	1,3,5-Trimethylbenzene	11.0	14.2	--
o	1,2,4-Trimethylbenzene	13.1	16.8	--
p	n-Decane	13.1	19.0	--
q	n-Undecane	30.7	--	--

Column: Squalane (5 parts), polyethylene glycol 400 (2 parts) on Chromosorb (100 parts).

The assignment of the hydrocarbons listed in Table 2 to the chromatographic peaks is considered to be reasonably firm. Retention volumes have been compared through the squalane column only but their correlation at the different temperatures serves to support the assignments. For more positive identifications, retention volumes must be matched on other partitioning agents of varied chemical structure. Those peaks attributed to specific hydrocarbons are undoubtedly not due solely to the hydrocarbons mentioned but most likely conceal small amounts of other materials with similar retention volumes. This is evidenced by the separation of smaller peaks from the larger ones as the column temperature was reduced (Figures 4, 7 and 9).

Quantitative Studies

The concentration of hydrocarbons in the atmosphere of the USS SKATE was estimated by measuring the areas under some of the chromatographic curves with a planimeter. Values obtained are listed in Table 3. These figures must be considered as estimates because of several factors leading to uncertainties. Measurement of sample volumes by means of a rotameter and pump was not satisfactory. Constant flow rates could not be obtained and the desired sample size could be only approximated. A suitable integral method of volume measurement is sought for future use.

The ionization detection system of the Pye chromatograph itself leaves much to be desired as a quantitative tool. The desensitizing effect of water caused the detector response to vary by as much as four or five times during the trip. To dry the system thoroughly between runs would have required an excessively long time. In order to minimize errors arising from traces of water, a standard solution of benzene in toluene was used for calibration of the detector response before each atmosphere sample. A difficulty with this method of calibration is that the maximum liquid sample that can be handled by the chromatograph without overloading the detector is on the order of 20-100 mmg. Reproducibility in measuring such small quantities is poor.

The limitation of the argon detector that was most difficult to deal with was the variation of response to different molecular species, especially among the lower molecular weight hydrocarbons. Aromatic hydrocarbons in particular give high responses because of the large cross sections of their molecules. For example, the response to benzene is almost twice that to the same quantity of a saturated hydrocarbon with a similar retention volume. To obtain an average

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Table 3

Hydrocarbon Concentrations in the USS SKATE Atmosphere Estimated by Gas Chromatography

Sample	Date	Location	Column Temp.	Hydrocarbon Conc. (mmg/l.)
1	10/23	Engine Room, Lower Level	75°	153
2	10/24	Engine Room, Upper Level	75°	155
3	10/25	Stern Room	75°	110
4	12/1	Forward Torpedo Room	75°	186
5	10/29	Nucleonics Laboratory	50°	143

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response to the various hydrocarbons present, a liquid sample desorbed from a carbon canister was taken as a standard. All measured areas from chromatograms of air samples were compared to the area produced by a known volume of the oil desorbed from carbon after normalization of each to the benzene standard. For more exact quantitative values, each peak must be identified and its area weighted by a response factor for that hydrocarbon.

Table 4 lists values of the concentrations of atmospheric hydrocarbons found by the Materials Laboratory at the New York Naval Shipyard by steam desorption of the carbon canisters exposed during the trip (9). It will be noted that the levels obtained by gas chromatography are consistently higher than these.

The combustion technique of passing air through a CO_2 absorber and thence through Hopcalite at 420-440°C and the subsequent infrared determination of the CO_2 yielded intermediate values to those obtained by carbon sampling and gas chromatography. Air samples for the combustion procedure were collected in the Nucleonics Laboratory located in the Stern Room. A measurement toward the end of the long submergence period showed the concentration of combustibles to be about 100 mmg/l. or 15 ppm as decane. After about a 5-1/2 hour period of ventilation on the surface, the combustibles fell to 68 mmg/l. (10 ppm). These combustibles include CO which remained at about 10 ppm during the submergence period. Substraction of the amount of CO_2 produced by the combustion of 10 ppm of CO leaves a value of 94 mmg/l. (14 ppm) total combustibles (as decane) before ventilation and 60 mmg/l. (9 ppm) afterwards. Oxygenated compounds most likely were absorbed by the Caroxite used for CO_2 removal. Methane would be expected to burn only partially on Hopcalite at the temperature and flow conditions used.

The presence of higher concentrations of hydrocarbons than indicated by carbon sampling is supported by the nature of the chromatograms obtained with low column temperatures and by an examination of the effluent from some carbon canisters during exposure. Chromatograms of air samples obtained aboard ship with column temperatures of 27° and 50°C showed considerably higher concentrations of hydrocarbons in the C_8 and lower ranges than were found in the oil samples desorbed from carbon and chromatographed under similar conditions. This may be seen by a comparison of chromatograms obtained at 50°C shown in Figures 7 and 8. Although these chromatograms do not represent hydrocarbon samples of equal size, the

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Table 4

Hydrocarbon Concentrations in the USS SKATE Atmosphere by Adsorption on Carbon (9)

Sample	Date	Submergence Time (Hrs.)	Hydrocarbon Concentration mmg/l.	ppm (as Decane)
1	10/19-20	3.5-15.5	71.7	11.3
2	10/20	19.5-27.5*	64.0	10.1
3	10/20-21	27.5-39.5	57.0	9.0
4	10/21	39.5-51.5	39.1	6.2
5	10/23	87.5-99.5	77.5	12.2
6	10/24	112-124	73.2	11.5
7	10/25-26	148-160	81.6	12.8
8	10/26-27	173-185	51.1	8.0
9	10/27	185-197	44.0	6.9
10	10/28-29	220-232	42.6	6.7
11	10/30	256-268	57.0	9.0
12	10/31	280 **	43.9	6.9

Location: Engine Room, Upper Level
Sampling Time: 12 hrs.

*Surfaced and ventilated for 45 min.

**Surfaced and ventilated after 3-1/2 hrs. of canister exposure. Remained on surface for 5-1/2 hrs.

greater abundance of volatile hydrocarbons is evident from a comparison of the relative areas under Peaks 1 through 10 of each curve with those under the remaining peaks. Peaks 8, 9 and 10 in Figure 7 are attenuated three times. Similar results were obtained with column temperatures of 27-28°C. In Figures 9 and 10 the total sample size of hydrocarbons represented by the chromatogram of the oil from carbon is much greater than that of the air sample. Peak 19 in each chromatogram was tentatively identified as an unresolved mixture of m- and p-xylene. Assuming that the xylenes were not eluted from the carbon during sampling, the two curves can be put on an equal sample basis by diminishing all peaks in Figure 10 by the ratio of the area of Peak 19 in Figure 10 to that of Peak 19, Figure 9. The higher concentrations of the more volatile hydrocarbons detected in direct air samples may easily be seen, especially after normalization of the curves to the xylene peaks.

Samples of the effluent from two of the Dorex carbon canisters were collected, concentrated and chromatographed by the same procedure used for the previous air samples. A chromatogram of the effluent from Canister No. 7 sampled immediately at the end of the twelve hour exposure period was similar in appearance to those obtained from submarine air itself except for slightly higher relative concentrations of octanes and lower boiling hydrocarbons (Figure 11). Integration of the area under the curve gave a value of 100 mmg/l. of hydrocarbon passing through the carbon bed. An examination of the exhaust from Canister No. 9 after 5-1/2 hours exposure indicated a residual concentration of 48 mmg/l. of hydrocarbons. The relative peak heights in this chromatogram (Figure 12) differed markedly from those from samples of the submarine air itself in that a decided enrichment of C_8 and lower molecular weight hydrocarbons was noticeable.

Loss of hydrocarbons from the Dorex canisters can be explained by both elution and air channeling. Elution of lower molecular weight hydrocarbons is evidenced by the relatively greater amounts of lower boiling materials passing through the canisters, especially after a short exposure period. The presence of higher molecular weight hydrocarbons such as decane and undecane in the canister exhaust and the similarity of those portions of the effluent chromatograms beyond Peak 5 to those of the submarine air itself are likely indications that air is channeling through the carbon bed. The significance of the different values of hydrocarbon concentrations in Table 4

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obtained at varying submergence time by carbon sampling is
not known in view of the apparent leakage through the cani-
sters. Variations in channeling among the canisters could
easily account for the differing hydrocarbon concentrations,
especially since Canister 9 indicated a level of only 44 mmg/l.
and yet gas chromatography estimated 48 mmg/l. passing through
the carbon after less than half of its normal exposure period.

Change in Hydrocarbon Composition with Time

A sufficient number of air samples was not chromato-
graphed under similar conditions aboard ship to draw any
conclusions as to changes in the hydrocarbon composition of
the atmosphere with submergence time. The oil layers steamed
from carbon canisters, however, did show some minor differ-
ences. The first canister exposed showed Peak 9 (m-p-xylene)
and Peak 10 (n-nonane, o-xylene) to be of about equal size
(Figure 13). In successive samples, Peak 10 decreased in
size relative to 9 until the ratio in Figure 14 was obtained
from the last canister exposed. Wide variations in the
heights of the first five peaks were found but no trends
with time could be established. It is believed that dif-
ferences among these first peaks were due to elution of
hydrocarbons in varying amounts in different Dorex canisters.

Present Status of the Gas Chromatographic Work

New chromatographic equipment, procedures and materials
are being explored for applicability to the submarine atmos-
phere problem including the possibility of direct shipboard
monitoring of contaminants by gas chromatography. The de-
velopment of capillary columns has provided greatly improved
separations over packed columns. Recent improvements in the
argon ionization detector such as the development of the
micro-detector and the triode and the use of tritium as an
excitation source give promises of sensitivities on the order
of a thousand times greater than can be obtained from the
simple detector used in the Pye Chromatograph. The flame
ionization detector appears particularly suitable for the
detection of low molecular weight hydrocarbons. A Jarrell-
Ash Capillary Chromatograph equipped with a tritium micro-
detector has been obtained and is being studied. The flame
ionization and triode detectors are interchangeable with the
standard micro-detector in this unit. It is hoped that the
increased sensitivity of the new detectors will eliminate
the need for the preliminary sample concentration step.

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SUMMARY

Hydrocarbon contaminants in the atmosphere of the USS SKATE were investigated aboard ship by means of gas chromatography in conjunction with a chromatographic concentration technique and by a catalytic combustion method. Hydrocarbons in air samples were collected by absorption in a chromatographic partitioning column at 0°C. Raising the column temperature to 100°C and backflushing the absorbed hydrocarbons directly into the analytical column of the chromatograph increased their vapor concentration some 20 to 50 times and made possible their direct chromatographic determination in air samples. Total combustibles in the atmosphere were determined by passing air cleansed of CO_2 through Hopcalite at 420-440°C and measuring the CO_2 produced with an infrared analyzer.

Both gas chromatography and the combustion technique indicated substantially higher hydrocarbon concentrations than were detected by Dorex carbon canisters exposed during the trip. Values obtained by carbon sampling ranged from 39.1 to 81.6 mmg/l. while concentrations of 110 to 186 mmg/l. were estimated by gas chromatography. The catalytic combustion procedure indicated 100 mmg/l. of combustibles (as decane) at the end of the long submergence period and 68 mmg/l. after a 5-1/2 hour ventilation period. Chromatograms obtained directly from air samples showed greater amounts of octanes and lower molecular weight hydrocarbons than did those from the oil desorbed from the Dorex carbon.

A chromatographic investigation of the exhaust from Dorex carbon canisters during exposure showed that hydrocarbons were lost both by elution of lower boiling hydrocarbons and by channeling of air around the carbon particles. The effluent from one canister after a twelve hour exposure period contained approximately 100 mmg/l. of hydrocarbons. Another passed 48 mmg/l. after only 5-1/2 hours.

Many of the hydrocarbons in the atmosphere were tentatively identified by comparing the retention volumes of chromatographic peaks produced by air contaminants with those of pure hydrocarbons. Hydrocarbons identified were those that are commonly found in high concentrations in petroleum fractions of comparable volatility.

CONCLUSIONS AND RECOMMENDATIONS

1. The use of gas chromatography for analysis of hydrocarbon vapors in submarine atmospheres was shown to have considerable promise. Further studies should be carried out to determine the feasibility of its use as a routine method.

2. With presently available gas chromatographic equipment it was found necessary to use procedures involving concentration of the contaminants in the atmosphere. It should be possible to improve such procedures considerably to increase total sensitivity and to make them more effective for submarine use. Techniques to analyze for lower molecular hydrocarbons which are now being lost appear feasible and are being pursued.

3. The field of gas chromatography is developing so rapidly that it can be foreseen that instruments now being developed might analyze for total hydrocarbons without recourse to concentration procedures.

4. The presently used carbon adsorption methods have been shown to detect less than half the quantity of hydrocarbons present. The more volatile hydrocarbon components in the submarine atmosphere are now partially or completely lost by elution. These include the more toxic aromatic hydrocarbons, benzene and toluene. Inherently, carbon sampling should give better results and because of its overall simplicity, studies to improve this technique are under way.

5. A very preliminary examination of a catalytic combustion method of analysis of total combustibles indicated that this method offers interesting possibilities, hence it is planned to study it further.

6. When laboratory studies show marked improvement in one or more of the items mentioned above it would be highly desirable to test such developments further aboard an operating submarine.

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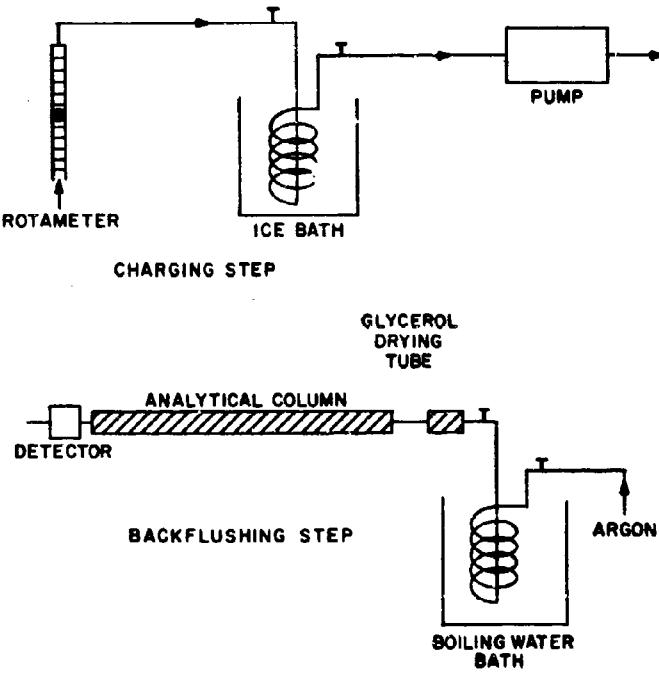
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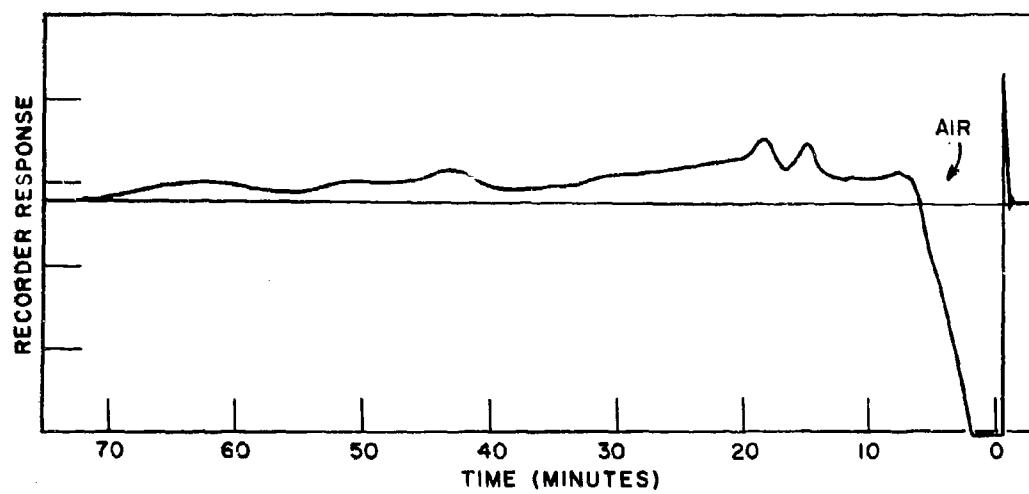
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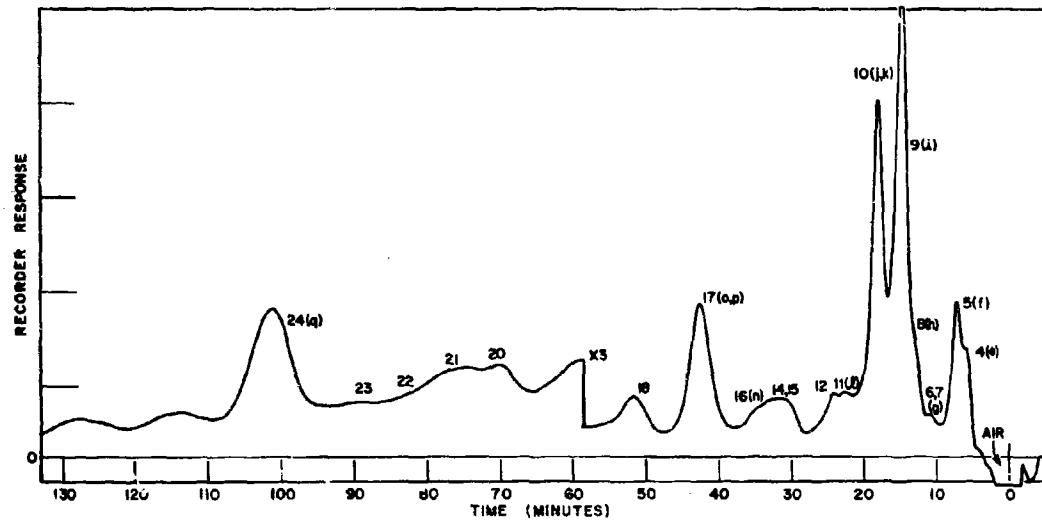
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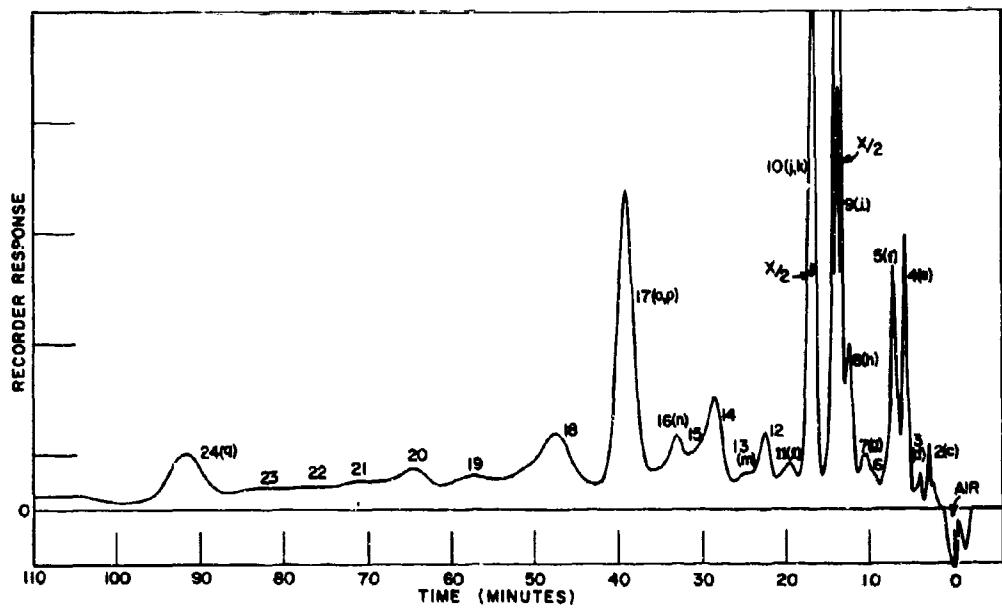
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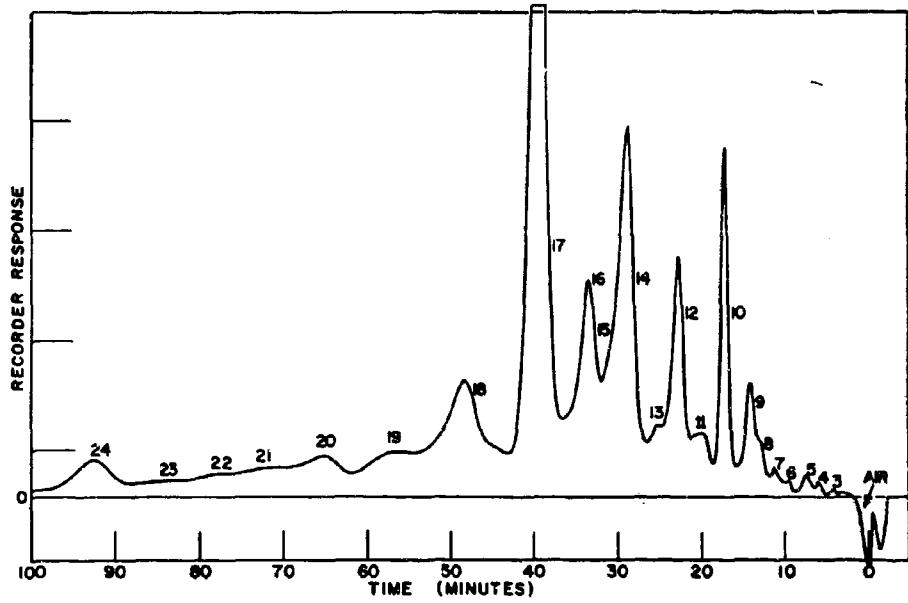

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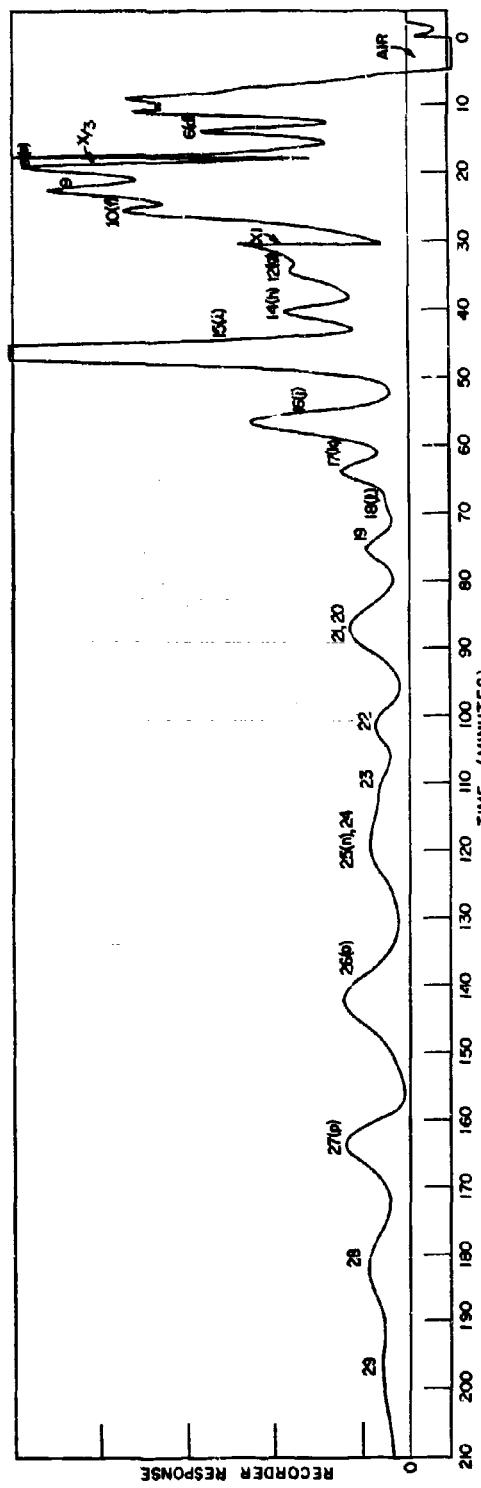
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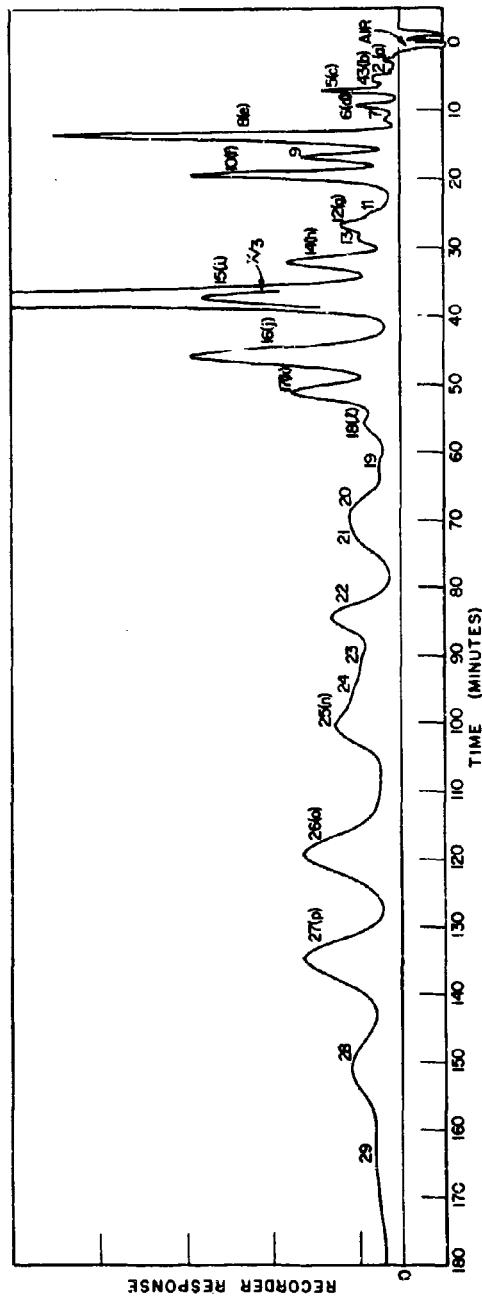
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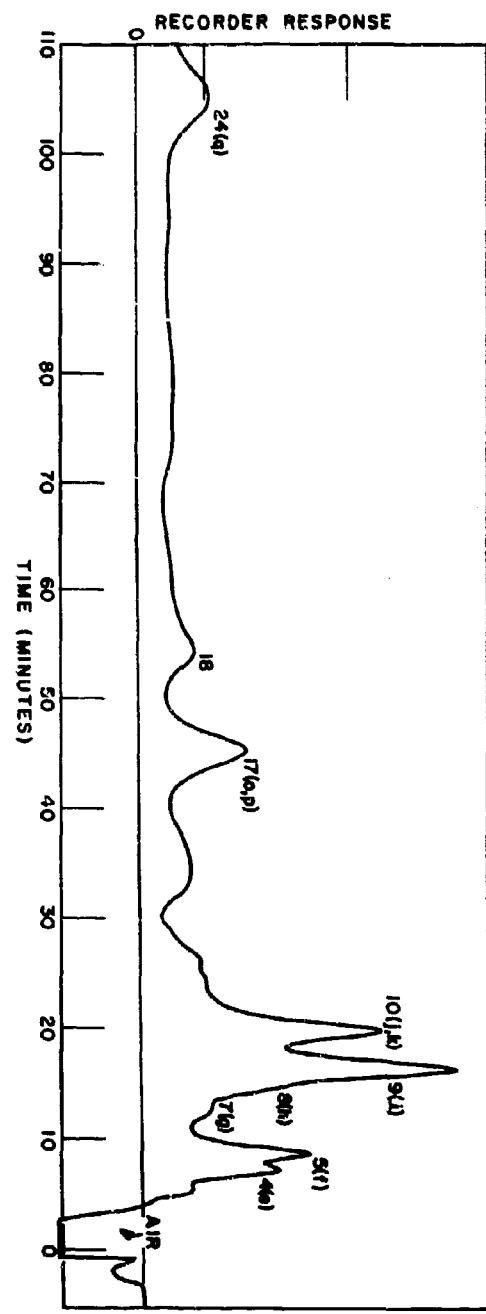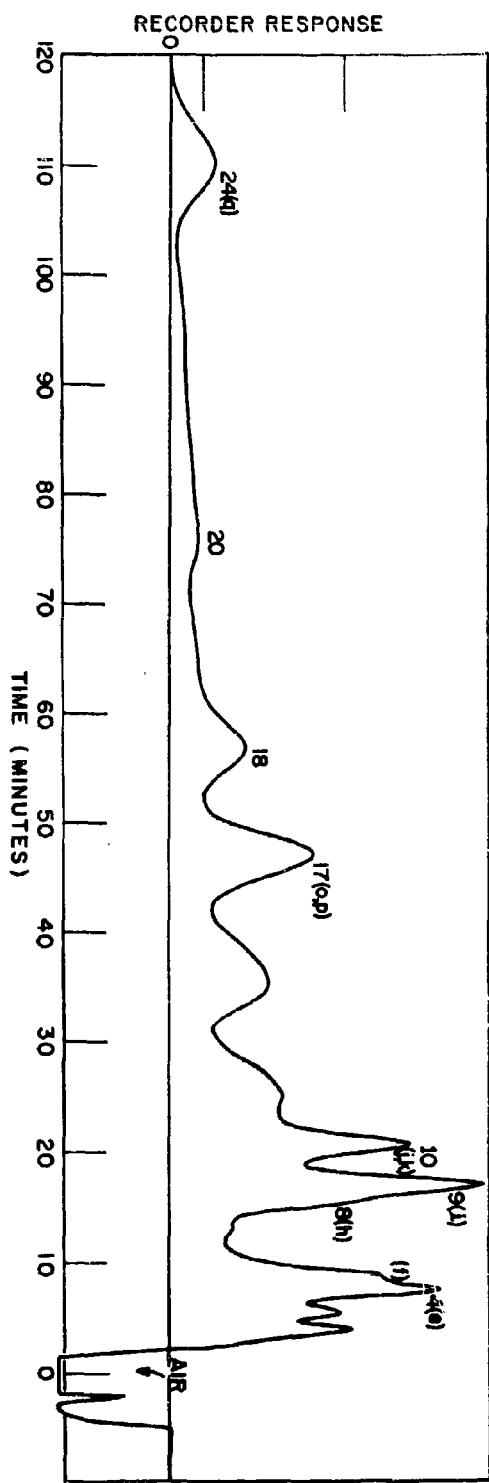
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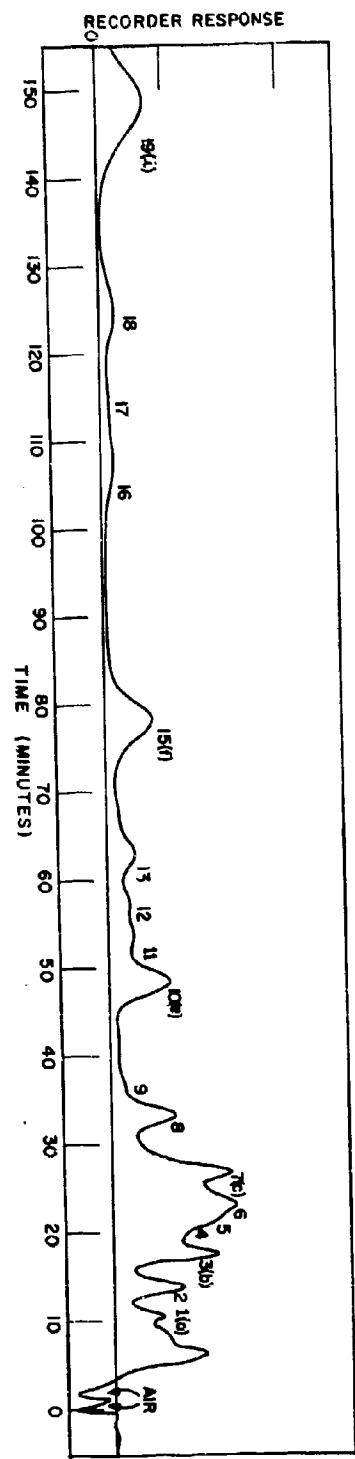
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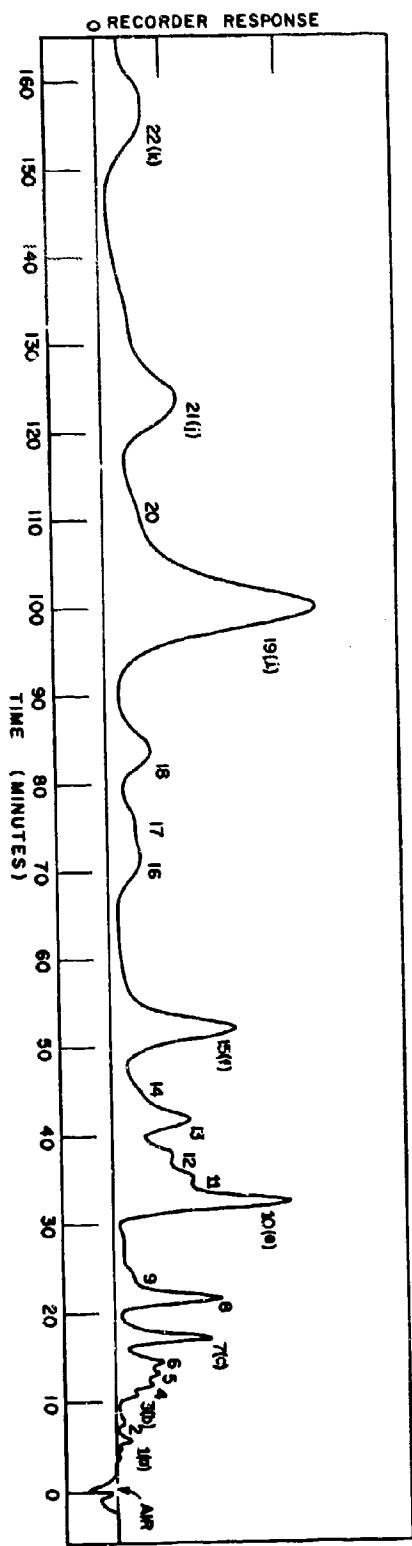
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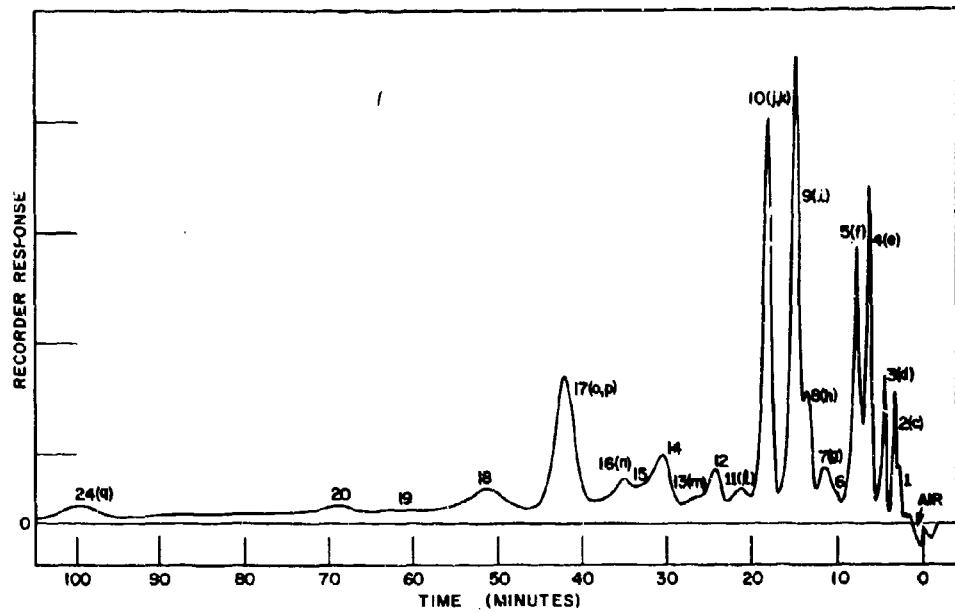
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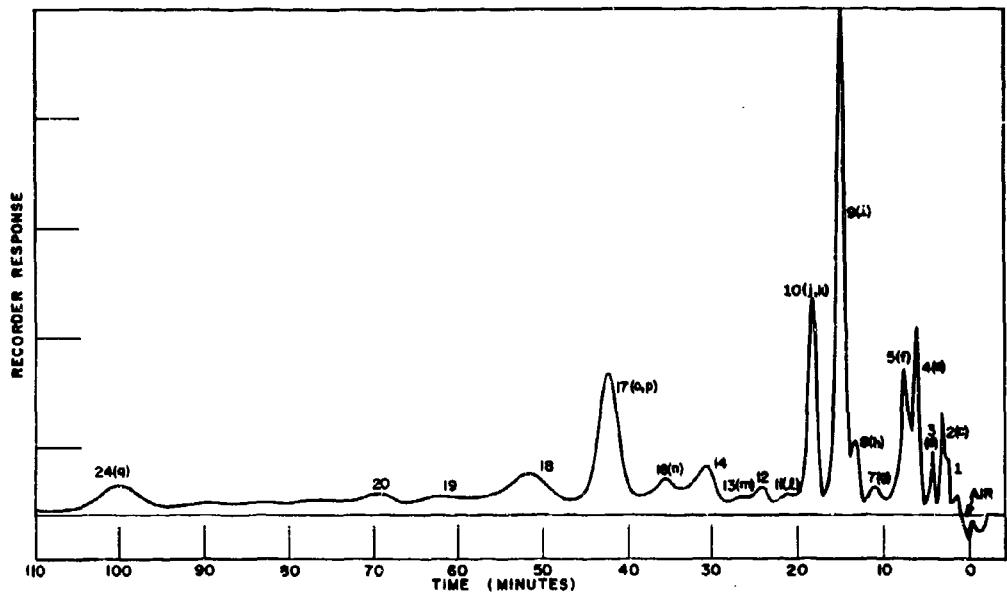
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